Available online at www.sciencedirect.com

Thermochimica Acta 411 (2004) 177–180

thermochimica acta

www.elsevier.com/locate/tca

Study on glass transition and crystallization kinetics of $Ge_xSb_{40-x}Se_{60}$ glasses by differential thermal analysis

Z.G. Ivanova[a,*], E. Cernoskova[b]

[a] Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria
[b] Joint Laboratory of Solid State Chemistry of Academy of the Czech Republic and University of Pardubice,
84 Studentska, 532 10 Pardubice, Czech Republic

Received 15 August 2003; accepted 18 August 2003

Abstract

Basic thermal parameters such as the glass transition and crystallization temperatures of bulk $Ge_xSb_{40-x}Se_{60}$ ($x = 15$, 20, 25, 27, 32 and 35) glasses have been determined by differential thermal analysis. The observed peculiarity in the variation of the glass transition temperature with the heating rate increase in the narrow range of average coordination number $Z = 2.65$–2.67 has been related to structural and chemical transitions. It has been established that especially the compositions at $x = 20$, 25 and 27 do not crystallize by the applied non-isothermal regime. Identification of the corresponding crystalline phases for the rest samples has been specified. The apparent activation energy of crystallization has values of $\sim$174 kJ mol^{-1}.

Keywords: Chalcogenide glass; DTA; Crystallization; Kinetics

1. Introduction

Thermal studies on chalcogenide glasses including glass transition and kinetics of crystallization are of particular interest from fundamental and practical view points [1]. These glasses are perspective infrared optical materials on the basis of good infrared transparency in the 8–12 μm range, high refractive index, low optical losses, etc. [2,3]. During the last years Ge–Sb–Se glasses and especially the $Ge_xSb_{40-x}Se_{60}$ family have been intensively investigated as regards their physical [4], optical [5], electrical [6] and elastic [4] parameters. Peculiarities in the compositional dependence of some properties at $Z \sim 2.7$ have been found. They are related to transition from a two-dimensional layered structure to a three-dimensional cross-linked network [7]. The threshold behavior at $Z \sim 2.7$ has been further considered by accounting the formation energy per atom of the glasses [8]. A nano-phase separation for explanation of the changes at this Z has also been suggested [9].

In our previous paper [10], such basic thermal parameters such as glass transition and softening temperatures, apparent activation energy of glass transition, specific heat capacity between glass and undercooled liquid and coefficient of thermal expansion of bulk $Ge_xSb_{40-x}Se_{60}$ glasses have been determined by differential scanning calorimetry (DSC) and thermomechanical analysis (TMA). Besides, peculiarities in some thermal [10] and physicochemical [11] parameters of these glasses at Z around 2.67 have been established. This paper is a continuation of the study on this family and considers the evaluation of the glass transition and crystallization by differential thermal analysis (DTA). The results concerning glass transition have been compared with those obtained by DSC and TMA.

2. Experimental

Glasses $Ge_xSb_{40-x}Se_{60}$, for $x = 15$, 20, 25, 27, 32 and 35 were synthesized by the well-known procedure [10] of heating at 950 °C from high pure (99.999%) elements. The differential thermal analysis was carried out using instrument R.M.I.-DTA 003 (Electronic Measuring Instruments, Czech Republic) at a non-isothermal regime in the temperature range 25–900 °C. Small quartz ampoules with powders (about 40 mg weight) were evacuated to 10^{-3} Pa and heated

---

* Corresponding author. Tel.: +359-2-7431256; fax: +359-2-9753632.
E-mail address: zojagiv@pronto.phys.bas.bg (Z.G. Ivanova).

0040-6031/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2003.08.014

with different rates of 5, 10, 15 and 20 K min^{-1}. The calibration was made with the help of In, Al, Zn, Pb and Sn in order to eliminate the difference between the temperature of the thermocouples in the furnace and in the vicinity of the sample. Pure Al_2O_3 was used as a standard. The identification of the corresponding arisen crystalline phases was made by X-ray diffractometer (Krystaloflex, Siements, Germany) with Fe-filtered Co Kα radiation and silicon (a = 5.43055 Å) as an external standard.

3. Results and discussion

The DTA data for the glass transition temperature (T_g) are in a good agreement with those obtained by DSC and TMA [10]. Fig. 1 shows that T_g average values increase from 220 to 330 °C with increasing x, which is logical having in mind that Ge is the highest melting element in the studied system. On the other hand, this parameter increases with the heating rate. A peculiarity in the compositional dependence of T_g is observed—its increase at higher heating rates in a very narrow range of $Z = 2.65$–2.67 becomes more rapid and at 20 °C min^{-1} the change in T_g is more than two times higher. In addition, a similar feature is observed as at the softening temperature, fragility and coefficient of thermal expansion [10], as well as at the microhardness, micro-voids volume and energy of their formation at $Z = 2.65$–2.67 [11]. Following different concepts for explanation of this fact [7–9], the observed feature can be connected with structural rearrangement expressing by phase transition and/or separation and accompanied by a chemical threshold.

It should be mentioned that the compositions at $x = 20$, 25 and 27 are very good glasses because their DTA thermograms do not show any crystallization effects after that of glass transition (Fig. 2). A very weak exothermal peak is observed at $x = 15$, and the samples that crystallize easy are those at $x = 32$ and 35, i.e. close to $GeSe_2$ (for comparison, the general DTA curve of the $Ge_{35}Sb_5Se_{60}$ composition is given in Fig. 2). The corresponding X-ray diffraction data are summarized in Fig. 3. At $x = 15$, only a Sb_2Se_3 phase crystallizes which is similar to the case at $x = 10$ [12]. At $x = 20$, 25 and 27, any crystalline phases are not found on the X-ray diffraction patterns (the weak traces at $x = 25$ could be attributed to GeSe phase). At $x = 32$, reflexes corresponding to c-$GeSe_2$ and c-GeSe phases appear, while at $x = 35$ predominantly a $GeSe_2$ phase crystallizes. In the latter two cases, lines connected with Sb are not registered, i.e. the Sb concentration is rather low that to form some separate phases. The $Ge_xSb_{40-x}Se_{60}$ family belongs to the non-stoichiometric Ge_2Se_3–Sb_2Se_3 line, i.e. it can be performed as solid solution of these binary components. This line is situated below the stoichiometric one in the Gibbs triangle and therefore the glasses are referred as "selenium deficient", i.e. Se–Se bonds are assumed not to exist.

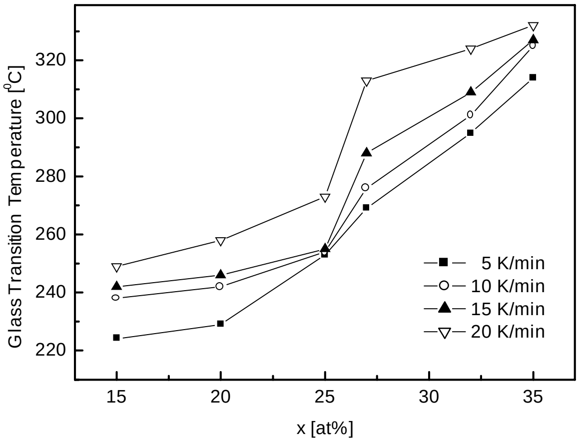

Fig. 1. Compositional dependence of T_g at different heating rates.

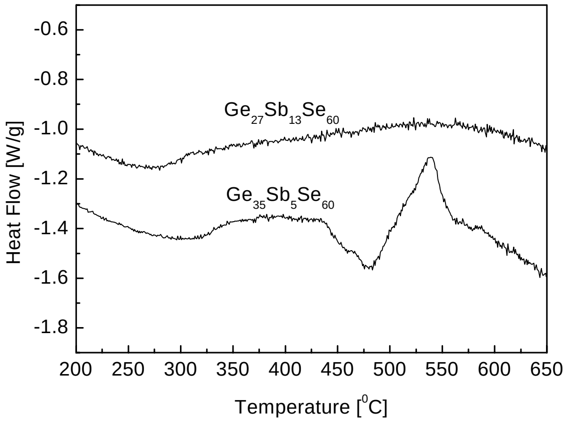

Fig. 2. DTA thermograms of glasses.

It is well known [13] that some glasses from the Ge–Sb–Se system do not crystallize non-isothermally due to their complicated structure. Stabilization of the glassy state is

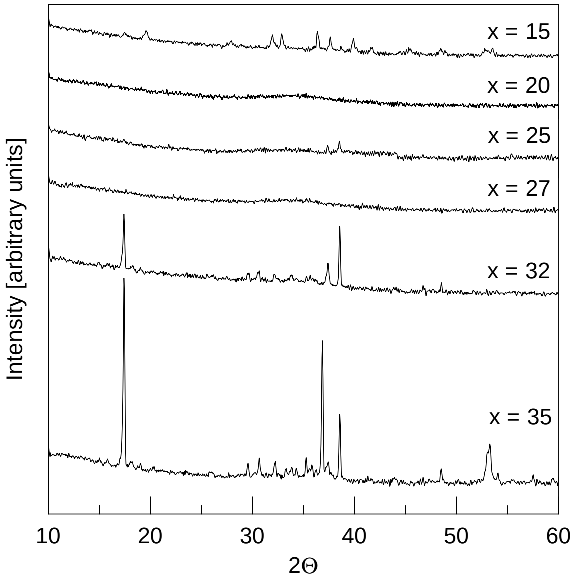

Fig. 3. X-ray diffraction patterns of the glasses studied.

Table 1
Temperature and activation energy of crystallization

x (at.%)	Z	T_c (°C)				E_a (kJ mol^{-1})
		5 K min^{-1}	10 K min^{-1}	15 K min^{-1}	20 K min^{-1}	
15	2.55	332.5	340.8	347.4	356.3	174.7 ± 27.0
32	2.72	432.3	449.7	460.1	467.2	169.8 ± 2.7
35	2.75	447.6	464.2	473.0	480.9	177.3 ± 3.7

observed especially at compositions with Ge content more than 20 at.% and Sb content up to 20 at.%. The possibility for creation of several different structural units (s.u.) makes difficult to separate individual crystal phases. Only a prolonged isothermal annealing of these glasses leads to separation of a stable crystalline phase whose composition corresponds to that of the predominant structural units in the glassy network (GeS_4 tetrahedra or Sb_2Se_3 pyramids). The distribution of the chemical bonds in the $Ge_xSb_{40-x}Se_{60}$ glasses shows [11] that at $x = 15$ the content of Ge–Se and Sb–Se bonds is equal. With increasing x, the fraction of Ge–Se bonds increases at the expense of Sb–Se ones and at $Z > 2.67$ the latter disappear. In particular, the ratio of [Ge–Se]/[Sb–Se] bonds at $x = 20$, 25 and 27 is 2, 8 and 9, respectively, i.e. the formation predominantly of basic glass-forming $GeSe_4$ s.u. is responsible for the very stable glassy state of these compositions. The appearance of so-called "wrong" homopolar Ge–Ge bonds at $x = 32$ and 35 leads to cross-linking of the glassy network and to a decrease of its connectivity. Consequently, ethane-like (Se_3Ge–$GeSe_3$) s.u. can be separated as a new nano-phase in the backbone of the glasses studied.

The crystallization peak is shifted to higher temperatures with increasing heating rate (Fig. 4), while the melting point remains almost the same (∼536 °C). The data for the crystallization temperature (T_c) of the studied glasses at $x = 15$, 32 and 35, obtained by the applied non-isothermal regime at four heating rates, are presented in Table 1. The average values increase from 344 to 467 °C with increasing Ge content.

The apparent activation energy of crystallization (E_a) is associated with the nucleation and growth processes that dominate the devitrification of most glassy solids. In general, separate activation energies must be identified with the individual nucleation and growth steps in a transformation, although they have usually been combined into an activation energy representative of the overall crystallization process [1]. In the applied non-isothermal method the sample is heated at a fixed rate, and the heat evolved is recorded as a function of temperature or time. This parameter is calculated by the Kissinger equation [14]. The obtained values of $E_a \sim 174\,\mathrm{kJ\,mol^{-1}}$ (Table 1) are two and more times lower than those of glass transition, determined from DSC and TMA by the same equation [10]. Consequently, the process of transition from glass to undercooled liquid requires rather higher activation energy than that of crystallization.

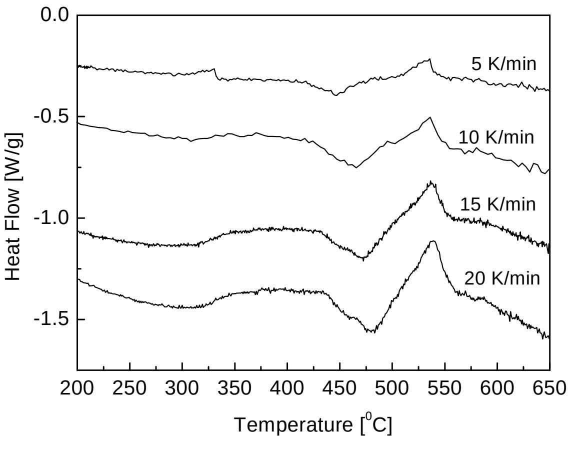

Fig. 4. DTA curve of $Ge_{35}Sb_{15}Se_{60}$ glass at different heating rates.

4. Conclusions

The obtained results from DTA study on $Ge_xSb_{40-x}Se_{60}$ glasses have shown that the observed rapid increase of T_g at higher heating rates in the narrow range of $Z = 2.65$–2.67, in particular with about two times at a heating rate of 20 °C min^{-1}, has been related to structural transformations in the glassy backbone. The T_c values vary from 340 to 470 °C and are higher by about 115 °C than those of T_g. It has been established that especially the compositions at $x = 20$, 25 and 27 do not crystallize non-isothermally at all. The crystallization of Sb_2Se_3, $GeSe_2$ and/or GeSe phases has been specified for the rest samples. The corresponding activation energy of crystallization is about two and more times lower than that of glass transition.

Acknowledgements

The authors thank Dr. K. Melanova (Joint Laboratory of Solid State Chemistry of Academy of the Czech Republic and University of Pardubice) for X-ray diffraction measurements and Dr. V. Pamukchieva (Institute of Solid State Physics, Sofia) for samples preparation. This work was partly supported by grant no. 303/99/0046 of Grant Agency of the Czech Republic.

References

[1] N. Rysava, T. Spasov, L. Tichy, J. Therm. Anal. 32 (1987) 1015.
[2] A.R. Hilton, D.J. Hayes, J. Non-Cryst. Solids 17 (1975) 339.

[3] J.A. Savage, P.J. Weber, A.M. Pitt, J. Mat. Sci. 13 (1987) 859.
[4] A.N. Sreeram, A.K. Varnshneya, D.R. Swiler, J. Non-Cryst. Solids 128 (1991) 294.
[5] M. Vlcek, L. Tichy, J. Klikorka, J. Mater. Sci. 24 (1989) 2508.
[6] S. Mahadevan, A. Giridhar, J. Non-Cryst. Solids 143 (1992) 52.
[7] K. Tanaka, Phys. Rev. B 39 (1989) 1270.
[8] L. Tichy, H. Ticha, Philos. Mag. B 79 (1999) 97.
[9] P. Boolchand, W.J. Bresser, Philos. Mag. B 80 (2000) 1757.
[10] Z.G. Ivanova, E. Cernoskova, V. Pamukchieva, J. Shanilova, Thermochim. Acta 345 (2000) 13.
[11] Z.G. Ivanova, V. Pamukchieva, M. Vlcek, J. Non-Cryst. Solids 293 + 295 (2001) 580.
[12] E. Cernoskova, Z.G. Ivanova, V. Pamukchieva, Thermochim. Acta 316 (1998) 97.
[13] Z.U. Borisova, Glassy Semiconductors, Plenum Press, New York, 1981, p. 278.
[14] H.E. Kissinger, Anal. Chem. 29 (1957) 1702.